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CALIFORNIA UNIV LOS ANGELES DEPT OF PHYSICS F/G 20/12  
CHARACTERIZATION OF INFRARED OPTICAL PROPERTIES OF LAYERED SEMI--ETC(U)  
MAR 82 R BRAUNSTEIN AFOSR-78-3665

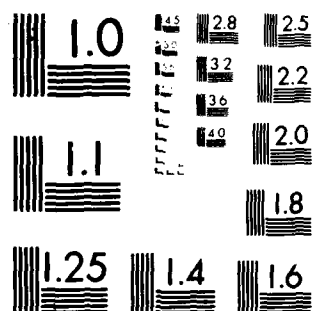
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The techniques of infrared wavelength modulation and the techniques of photo-induced-transients-spectroscopy were used to study the electronic structure and lattice dynamics of semiconductors. These studies have included: 1) the assessment of homogeneity of doping and strain in layer semiconductors, 2) the electronic structure of deep levels by wavelength modulation, 3) study of deep levels by photoinduced transients spectroscopy. The present work was primarily directed toward GaAs and Si.		

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Characterization of Infrared Optical  
Properties of Layered Semiconductors

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Prepared by:

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## Research Objectives

The broad objectives of this research program are to extend our understanding of the electronic structure, lattice dynamics, and interactions which occur in layered compound semiconductors. The electronic structure of surfaces, free-carrier screening effects on final state interactions, structure of oxide-semiconductor interfaces and interface surface phonons are studied by optical means. These interactions have a bearing on the utilization of ultra small electronic devices and the results of these studies contribute to programs involved in the synthesis of layered heterostructured compound semiconductors. Several unique instruments are employed to encompass the spectral range of inter-band, intra-band, impurity levels and lattice dynamical interactions. A wavelength modulated spectrometer is utilized to determine the spectral distribution of absorption or reflection at levels of  $10^{-5}\text{cm}^{-1}$  in the spectral range 6.0 - 0.05 eV. Low frequency modes are observed by Rayleigh, Brillouin and Raman backscattering utilizing a tandem multi-pass Fabry-Perot interferometer of high contrast ratio and extended free spectral range to  $100\text{ cm}^{-1}$ .

## Status of Research Summary

During the recent period, we have directed our program activities toward the study of deep levels and interfaces of GaAs, and other semiconductors. In these studies the techniques of infrared wavelength modulation, Rayleigh-Brillouin-Raman backscattering and photoinduced transients spectroscopy were employed. In earlier phases of this general program to characterize the infrared properties of highly transparent solids, the activities centered on insulators. Using our infrared wavelength modulation system, for the first time, the continuous spectral distribution of the absorption of highly transparent solids at levels of  $10^{-5}\text{cm}^{-1}$  were measured on materials of laser window interests. These studies enable us to identify volume and surface contaminants responsible for the absorption in the 0.2 - 12.0 micron range. In addition, using our multi-pass tandem Brillouin spectrometer, we studied the scattering from single and polycrystalline alkali halides to determine the effects of grain boundaries and impurity pinning at dislocations.

We have successfully demonstrated the power of the above techniques to the study of the electronic structure and lattice dynamics of semiconductors. This activity has included: 1) the assessment of homogeneity of doping, alloy composition and strain in layer semiconductors, 2) the electronic structure of deep

levels by wavelength modulation, 3) study of deep levels by photoinduced transients spectroscopy; 4) Raman-Brillouin studies of oxides.

The progress in these areas include:

a) Strain in ion implanted GaAs due to Be, Sb, S, In and doubled implanted Sb and Be was studied by the shift in the  $L_3-L_1$  critical point using wavelength modulation.

b) We have shown that we have the capability of detecting oxygen in silicon at levels of  $3 \times 10^{12}/\text{cm}^3$  compared to conventional methods which are limited to  $5 \times 10^{15}/\text{cm}^3$ . The kinetics of oxygen under heat treatment was studied.

c) Using our infrared wavelength modulation system, we can detect a fraction of a monolayer of SiO<sub>2</sub>; studies of oxides on Si and GaAs, were pursued which enabled us to detect OH<sup>-</sup> in oxides in GaAs.

d) Deep levels in high purity Si and semi-insulating GaAs were studied by wavelength modulation. These optical measurements have a sensitivity comparable to DLTS and enables us to determine optical cross-sections of deep levels. The deep levels observed in Si seem to be associated with vacancies. Fine structure observed in semi-insulating GaAs have a bearing on the various oxidation states of Cr and O.

e) Photo-induced-transients- spectroscopy (P.I.T.S.) was employed to study the deep levels in GaAs grown by M.B.E., L.P.E. and other synthesis techniques. The activation energy and recombination rates of deep levels were determined.

The following work has been completed and publications are to appear or are in preparation:

1. "Optical Studies of Surface Plasmon of  $n^+$  Silicon" - P. F. Robusto and R. Braunstein, Phys. Status Solidi (b) 107, 127 (1981).
2. "De-Correlation Technique for Separating Drude and Interband Parameters by Wavelength Modulation", R. Stearns, M. Burd and R. Braunstein (in preparation).
3. "Optical Measurement of the Surface Plasmon of Cu," P. F. Robusto and R. Braunstein, Phys. Status Solidi (b) 107, 443 (1981).
4. "Deep Levels of Cr in GaAs" R. K. Kim and R. Braunstein (in preparation).
5. "Gating Circuit for  $\lambda$ -Modulation Spectrometer," R. Stearns, J. Steele and R. Braunstein (in preparation).

6. "Optical Properties of  $\beta'$  - AuZn" R. Stearns and R. Braunstein (in preparation).
7. "Wavelength-Modulated Spectra of the Optical Properties of  $\beta'$  Cu<sub>x</sub> Zn<sub>1-x</sub> at the  $\beta' \rightarrow \alpha + \beta'$  Phase Transition," R. Stearns and R. Braunstein (in preparation).
8. "Oxygen and Deep Levels in High Purity Silicon," R. K. Kim and R. Braunstein (in preparation).

Personnel Associated With Project:

R. Braunstein	Principal Investigator
B. Bobbs	Ph.D. Candidate
M. Burd	Ph.D. Candidate
D. Deal	Ph.D. Candidate - Completed January, 1982
M. Eetemadi	Ph.D. Candidate
R. K. Kim	Ph.D. Candidate

Status of Research:

Wavelength Modulation, Photo-Induced-Transients and Light Scattering

We have modified a number of grating monochromators to extend the wavelength modulation techniques into the infrared. The modulation of the wavelength is accomplished by oscillating an output diagonal mirror similar to the system employed in the visible; this method of modulation is equally good for any wavelength in the spectral range of the monochromator and the amplitude of wavelength modulation can be continuously varied up to  $\Delta\lambda/\lambda \sim 10^{-2}$ . The wavelength modulation technique yields essentially the energy derivative of the absorption coefficient. To obtain the absolute value of the absorption coefficient, one numerically integrates the observed derivative spectra and the constant of integration is supplied by a direct loss measurement in the same apparatus at a fixed wavelength where the absorption can be measured with good precision.

Figure 1a shows a block diagram of the system implementing the above operation, which is under microprocessor control. The detector presently employed

for the infrared is a liquid nitrogen-cooled PbSnTe with a globar source for the spectral region from 2 to 12 microns. This system can be used equally well in the ultraviolet, visible and infrared regions with appropriate changes of sources, gratings and detectors.

We have used our wavelength techniques to determine shifts in various critical points as a function of doping and strain in several semiconductors.

Strain in chemically vapor deposited layers of Si on sapphire were detected by examining the 3.4 eV critical point. A polarization dependence of the shift was observed indicating an anisotropic strain exists in 4700 Å to 1900 Å layers in Si. It was possible to correlate the observed strain with the temperature of preparation of the layers.

Strain in ion implanted GaAs was readily observed by our technique. The shift in the  $L_3-L_1$  critical point due to various implanted species such as Be, Sb, S, In and double implanted Sb and Be were observed; the implanting flux was of the order of  $10^{13}/\text{cm}^2$ . It is surprising that band structure changes were observed by such low levels of implanting either attesting to the sensitivity of our techniques or the havoc wrought by the processing! However, mobility measurements on these samples could not reveal evidence for strain. Compared to unimplanted GaAs, positive and negative shifts of the energy of the critical point was observed, indicating that we are able to distinguish contraction or expansion of the lattice. For liquid phase epitaxial layers, we have been able to observe changes in the position of the critical point which can be correlated with the size of the donors or the acceptors.

Figure 1b shows the integrated derivative spectra of the state of the art KBr used for laser windows which has absorption at levels of  $10^{-5}\text{cm}^{-1}$ . Analysis of these spectra and other alkali halides has enabled us for the first time to identify volume and surface contaminants.

Using our infrared modulation system, we have been able to detect the 9 micron SiO absorption band in a 10 Å layer of native oxide with a signal-to-noise of 100/1, indicating that we have the capabilities of studying a fraction of a monolayer of adsorbed spectra. An example of this band is shown in Fig. 1c.

Oxygen and carbon play a ubiquitous role in Si device fabrication which is still not fully understood. The limit of detectability of oxygen by



conventional optical techniques is 0.1 ppm or  $\sim 5 \times 10^{15}/\text{cm}^3$ . We have shown that we have the capability of detecting oxygen at levels of  $3 \times 10^{12}/\text{cm}^3$ , if anyone has produced such an oxygen free sample! In all floating zone crystals of Si examined, we were able to detect oxygen at levels of  $10^{14}/\text{cm}^3$  by measuring the derivative of the absorption of the bulk 9 micron Si-O vibrational band relative to a known standard.

As an example of the sensitivity of infrared wavelength modulation technique for looking at levels within the energy gap, Fig. 4 shows some results for high resistivity GaAs. Normally, one observes a single peak at  $\sim 0.78$  eV as has been reported many times in the literature and has been identified as due to Cr. The richness of the fine structure should be noted; these structures have a bearing on the oxidation states of Cr in GaAs. This data was obtained by measuring the optical derivative of the absorption; however, for display purposes we have integrated the derivative data. It should be noted the vastly expanded scale of the figure, changes in absorption of  $10^{-2}\text{cm}^{-1}$  are significant in this data. Measurements are performed on a 20 mil thick sample. It was possible to observe differences in the spectra along sections of the wafer, indicating inhomogeneties of the impurities.

The Brillouin scattering apparatus that we have assembled for the study of surface phonons is shown in Fig. 2a. The arrangement is a conventional Brillouin scattering spectrometer; however, the unique feature of the Fabry-Perot interferometer is that it is a vernier tandem interferometer that can be used in multi-pass configurations yielding a contrast ratio of  $10^{10}$  with a free spectra range of 120 GHz. Figure 2c shows Rayleigh-Brillouin back-scattering spectra of GaP of unknown crystal orientation illustrating the contrast ratio for observing the longitudinal and transverse modes out of a large Rayleigh background. Figure 2b is an example of Rayleigh-Brillouin scattering from a polymer. This sample was a freely suspended clear plastic polyethylene sandwich wrap, 13  $\mu\text{m}$  thick, purchased from the local Safeway Supermarket! We use this example merely to illustrate that we have the capabilities of studying the elastic properties of various photo and electro-resists and oxides on semiconductors for lithographic application at the sub-micron thickness level as well as the surface phonons on semiconductors.

Photoinduced transients spectroscopy (P.I.T.S.) techniques involve the detection of current decay due to the emission of trapped carriers after illumination by chopped band gap light. In brief, excess electron-hole pairs are optically generated in high-resistivity semiconductors by an intrinsic light pulse. After the light pulse, a transient current due to de-trapping of carriers from deep levels can be observed between two ohmic electrodes. The current decay is usually sampled at two fixed time intervals as a function of temperature; the procedure is repeated for a range of sampling times. By plotting the difference logarithmically as a function of temperature, peaks occur when the trap emission rate is equal to the sampling rate in the case of discrete levels. Hence by varying the sampling time and observing the peaks at a given temperature, the trap energy and thermal emission cross sections of the deep levels can be determined. Such a procedure which has been employed by previous investigators is extremely time consuming.

In our system, the apparatus is controlled by a LSI/11/23 computer which controls the light pulse, controls and varies the temperature, and digitizes the complete current transient and computes, on-line, the parameters of the deep levels. Figure 3a shows a block diagram of our system. This system is a great time saver since for a single temperature sweep 100 time intervals are measured and signal averaged. Since the complete transient is measured, rather than the usual double-gate measurement which assumes an exponential decay, we can distinguish non-exponential decays due to multiple levels.

Figure 3b shows data obtained with the above apparatus for an L.P.E. layer.  $I(t_0) - I(t_2)$  was taken for  $t_1 = 30$  milliseconds and  $t_2 = 450$  milliseconds, the bias field was 30 V between two contacts separated by 3 mm. It should be noted that the data in the lower part of the figure reveal a large peak at  $\sim 260$  K while structure between 95 K and 170 K are obscured by the digital noise. However, in the upper curve of the figure by expanding the scale factor, structures between 95 K and 170 K are readily observed. We have observed different levels in samples of different origins.

Toward the latter phase of this report period, we directed our attention to the problems of deep levels in GaAs which have relevance to low noise amplification, generation and detection of high frequency radiation. These studies utilized our wavelength modulation and P.I.T.S. techniques.

The following are two abstracts submitted for presentation at the 16th International Conference on the Physics of Semiconductors and the 1982 International Symposium on Gallium Arsenide and Related Compounds:

Deep Level Derivative Absorption Spectroscopy of GaAs

R. Braunstein, R. Y. Kim, University of California at Los Angeles,  
and D. Matthews and M. Braunstein, Hughes Research Laboratory.

We have demonstrated that infrared wavelength modulation absorption can detect deep impurity concentrations at levels of  $10^{12}$ - $10^{14}/\text{cm}^3$  in semiconductors; previously, it had only been possible to study such concentrations by junction DLTS techniques and consequently it was not possible to observe absorption thresholds and excited states of deep impurities. An extensive study has been made on semi-insulating GaAs substrates in the spectral region from 0.5 - 1.4 eV prepared by various growth techniques. We have observed extensive fine structures with variations in absorption coefficients -  $\Delta K \sim 10^{-1} - 10^{-2} \text{ cm}^{-1}$  out of a relatively smooth background absorption of  $1 - 2 \text{ cm}^{-1}$ . Previous conventional optical absorption measurements reported in the literature have revealed a few plateau structures, indicating that they have only observed the envelope of absorption in this region. The relative magnitudes and the detail structure at 300 °K varies from sample to sample, although the dominant structures are similar. Marked differences in the temperature dependence of the structures are observed in different samples in the temperature range 300-78°K. The results will be discussed in terms of excited states of various deep levels. In addition, the optical absorption results will be compared with the electrically active centers studied by photo-induced-transient-spectroscopy on the same samples.

Abstract for Presentation at the 1982 International Symposium on Gallium Arsenide and Related Compounds.

Characterization of Deep Levels of GaAs by: Wavelength Modulation and Transient Photocurrent Techniques. R. Braunstein, M. Burd, University of California, at Los Angeles. And D. Matthews, Hughes Research Laboratory.

The rapid characterization of a "winning" device performance semi-insulating substrate is of prime importance for GaAs FET technology. The parallel techniques of infrared wavelength modulation absorption and photo-induced transient spectroscopy were employed to study deep levels in semi-insulating GaAs. Deep level derivative absorption is capable of detecting impurity concentrations at levels of  $10^{12}$ - $10^{14}/\text{cm}^3$  in high-resistivity material where junction DLTS techniques are not applicable. A study was made on substrates prepared by various growth techniques in the spectral region from 0.4 - 1.4 eV. Extensive fine structure was observed at 300°K in all samples, with differences in the relative magnitudes of the spectral features related to the method of crystal growth; marked differences are observed in the temperature dependence of the structures. These structures are observed with variation in absorption coefficients,  $\Delta K \sim 10^{-1} - 10^{-2} \text{ cm}^{-1}$  out of a relatively smoothly varying background absorption of  $1\text{-}2 \text{ cm}^{-1}$ . In addition, photo-induced transient spectroscopy techniques were employed on the same samples to determine trap energies and thermal emission rates. This system is controlled by an LSI/11/23 CAMAC based computer which controls the light pulse, sample temperature and digitizes the complete current transient. Since the complete transient is measured, rather than employing the usual double-gate technique, it is possible to distinguish non-exponential decays due to multiple levels. These measurements are performed on device test pattern structures. Different levels characteristic of sample preparation and substrate growth techniques are observed. The relationship between observed absorption fine structure, trap levels and device performance will be discussed.

Scientific Interactions:

Although the UCLA program is self-contained, we have maintained close communication with materials synthesis groups at the Hughes Research Laboratory, the Air Force Avionics Laboratory and other laboratories involved in the synthesis of layered semiconductors. These interactions included exchange of samples and technical discussions of the experimental and theoretical results of the UCLA group.

A seminar entitled: "Infrared Wavelength Modulation on Highly Transparent Solids" was given at the Laser Institute at USC on October 8, 1981. A seminar was given at the Hughes Research Laboratories on "Wavelength Modulation and P.I.T.S. on Semiconductors" on January 7, 1982.

## APPENDIX

## FIGURES

- Fig. 1. Infrared Wavelength Modulation System and Examples
- Fig. 2. Vernier Tandem Fabry-Perot System and Examples
- Fig. 3. Photo-Induced Transients Spectroscopy (P.I.T.S.) Apparatus and Examples
- Fig. 4. GaAs Wavelength Modulation Results

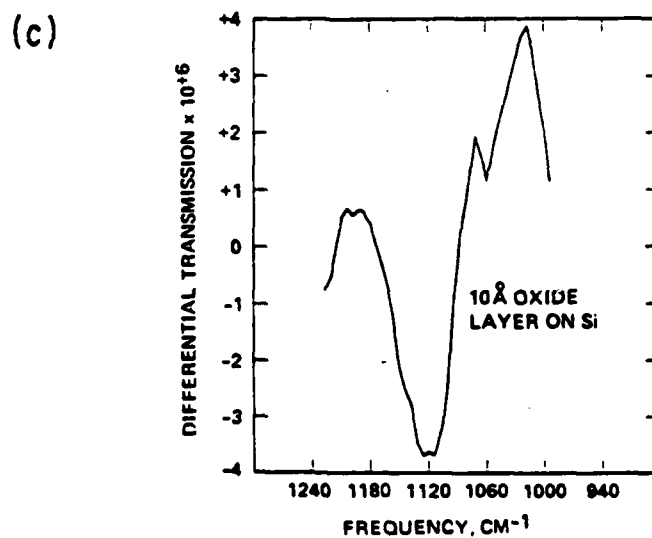
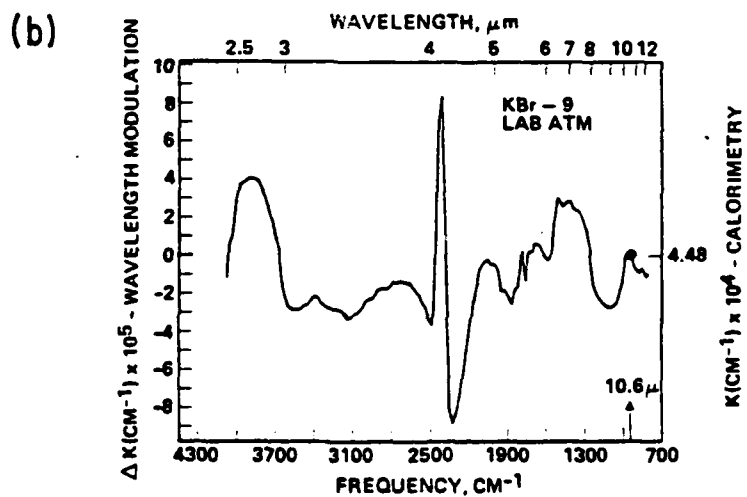
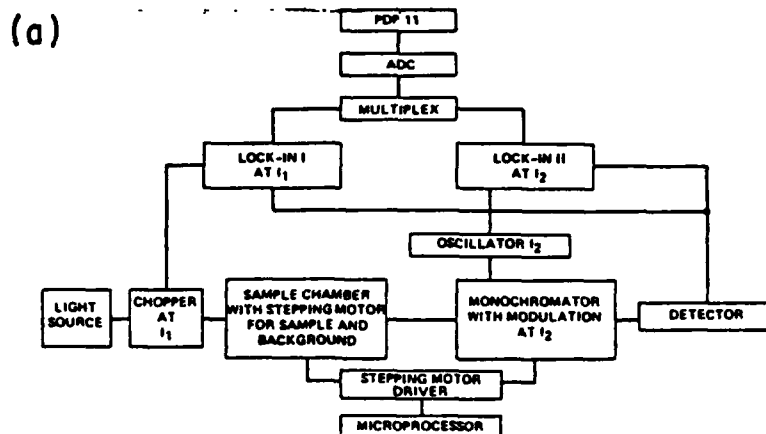


Fig. 1



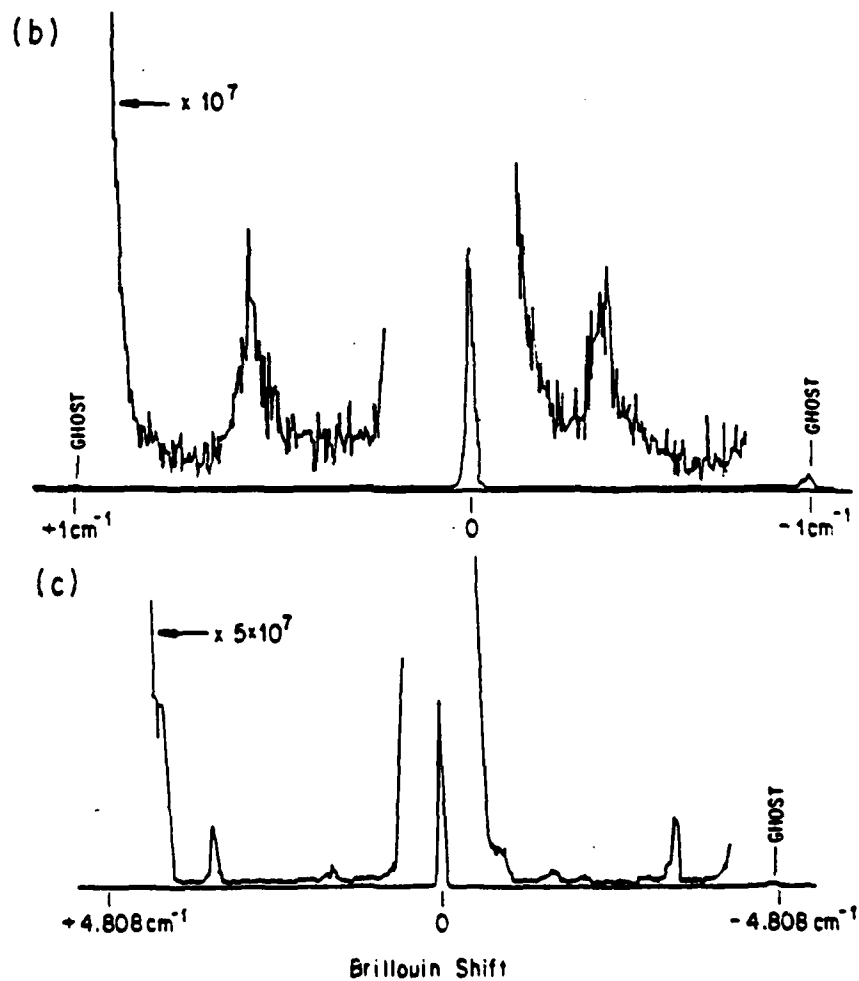
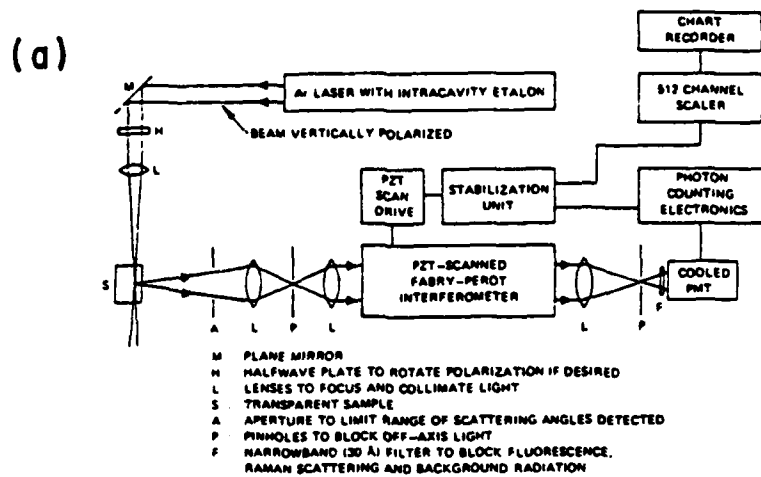


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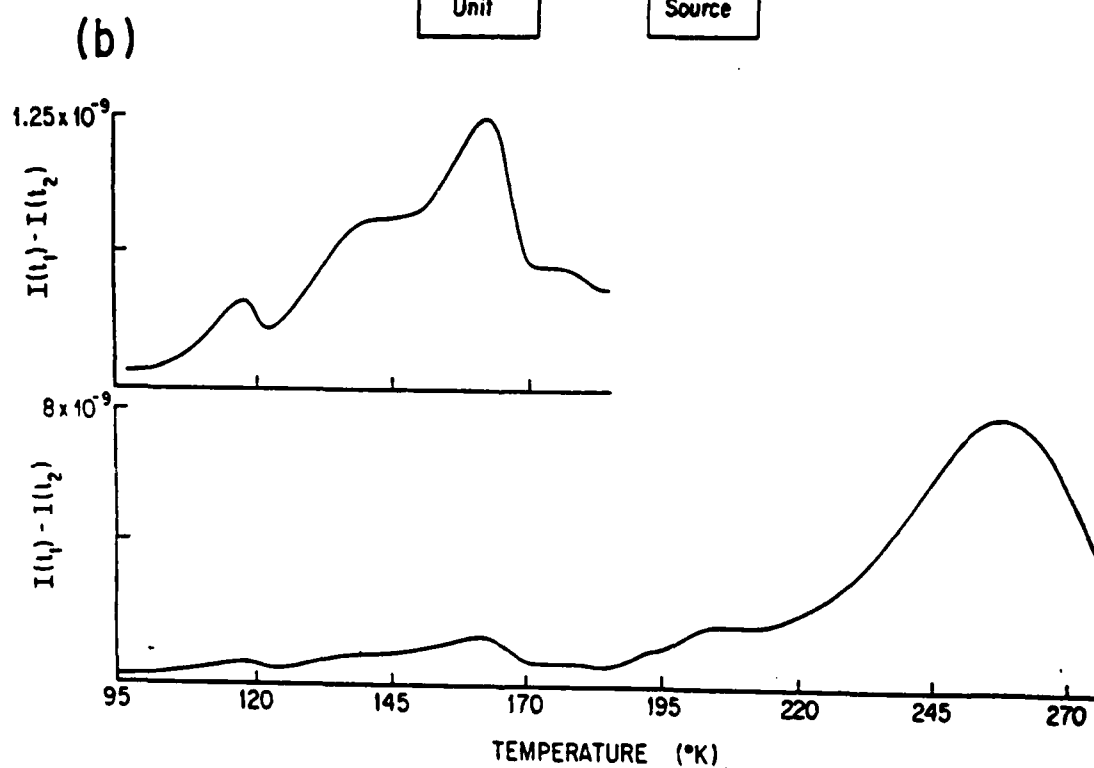
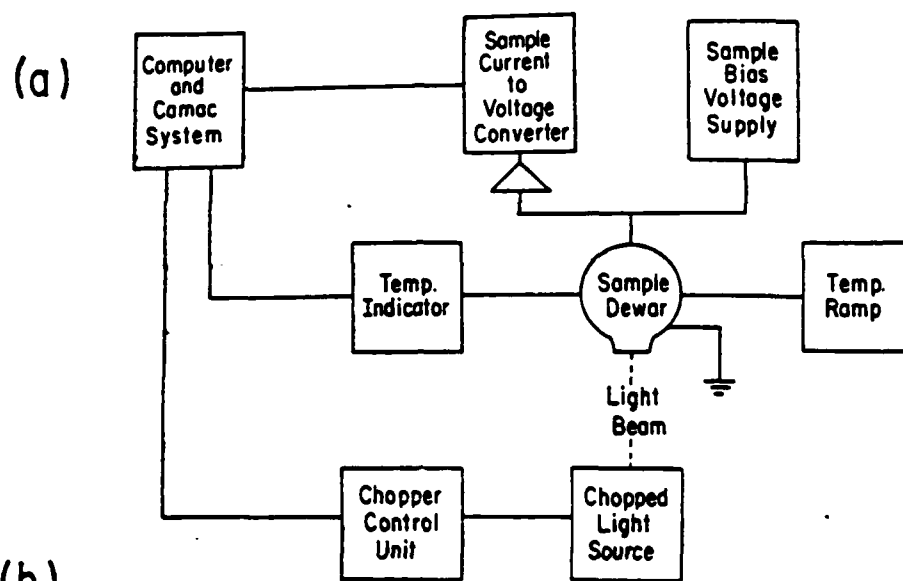


Fig. 3

# Absorption Coefficient of GaAs:Cr

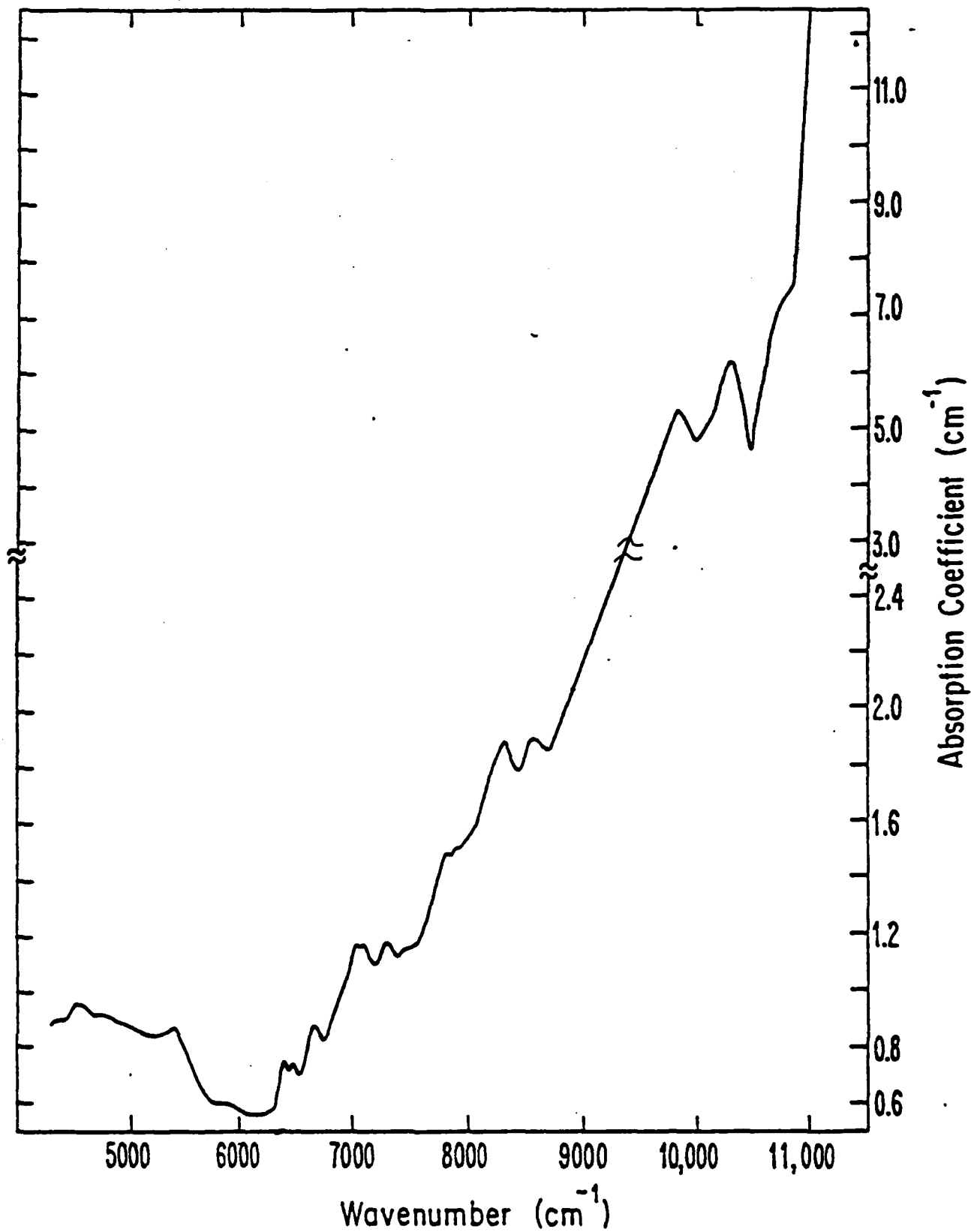


Figure 4

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